Synthesis of boron subnaphthalocynine chloride and axially-substituted subphthalocyanine

Samuel Headlee, Semen Dudkin, Viktor Nemykin

University of Minnesota- Duluth, Department of Chemistry, Duluth MN

Abstract:

Axially-substituted subphthalocyanine and boron subnaphthalocyanine chloride were synthesized to investigate their electronic properties as donors in donor-acceptor systems. These donor-acceptor systems were made in an effort find an efficient way to harvest solar energy and mimic natural photosynthesis.

Introduction:

Recently, many efforts have been made to mimic the natural photosynthetic reaction center with artificial systems. The general aim of this research is to develop efficient solar cells to harvest solar energy[1]. This goal has been approached in several ways. Several chemists have explored donor-acceptor structures in an effort to mimic the photo-induced energy increase and electron transfer processes found in natural photosynthesis. In order to make these donor-acceptor systems effective, they need to be efficient. In order for a donor-acceptor system to be efficient, a long-lived charged state, a large band gap, and effective electron transport is needed. This can be achieved through the fine-tuning of the chromophore using a variety of synthetic methods[2]. Several classes of chemicals have been used as donors including porphyrins, subphthalocyanines. This research focuses on the donors in donor-acceptor systems, specifically subphthalocyanines. The subphthalocyanine structures are substituted in various ways with the goal of achieving more efficient electron transfer and longer charge-separated states.

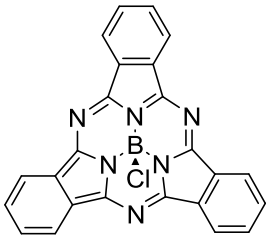


Figure 1: Structure of boron subphthalocyanine chloride, the base compound from which substituted subphthalocyanines are synthesized in an attempt to increase the desired electronic properties.

Methods:

All commercial reagents were ACS grade and were used without further purification. All reactions were performed under dry argon atmosphere with flame-dried glassware. Dry toluene was obtained by distillation over sodium, ferrocenylmethanol were prepared according to the literature procedures[3]. UV-vis data was obtained on Jasco-720 spectrophotometers.

Synthesis axially-substituted subnaphthalocyanine[4]

Boron subphthalocyanine chloride (50 mg, 0.116 mmol), silver triflate (37 mg, 0.148 mmol), and ferrocenylmethanol (50 mg, 0.233 mmol), were dissolved in 3 mL dried toluene in a Shlenk flask. The reaction mixture was stirred at rt for 2.5 h. . The crude product was separated via column chromatography (SiO_2, toluene: THF (5:2, v/v)). The first pink fraction was collected and evaporated via rotary vacuum evaporation. The yield was 12 mg (17%).

UV-vis (toluene): λ_{max}, nm (relative intensity): 565 (1.0), 535sh, 525sh.

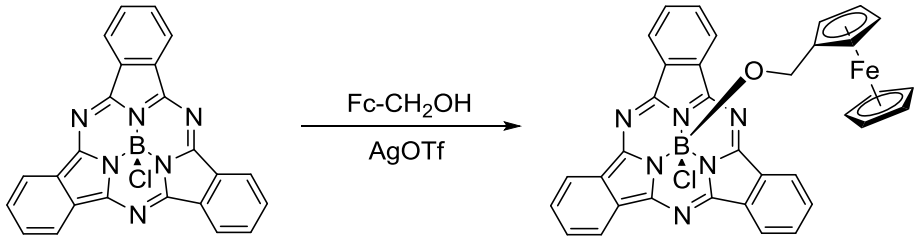
Synthesis of boron subnaphthalocyanine chloride[5]

Naphthalene-2,3-dicarbonitrile (500 mg, 2.81 mmol), BCl_3 (210 mg, 1.8 mmol) and 17 mL of *o*-xylene were added to a Shlenk flask. The reaction mixture was heated to 180^0C for 1.5 h and cooled to rtLC. The crude product was separated via column chromatography (SiO_2, toluene). The solvent was evaporated via rotary vacuum evaporation to give a blue solid. The yield was 280 mg (53%).

UV-vis (toluene): λ_{max}, nm (relative intensity): 655 (1.0) 595sh, 327 (0.45)

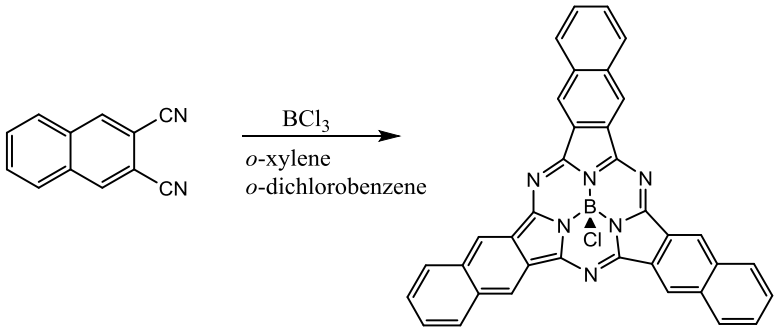
Results/Discussion:

Axial substitution of boron subphthalocyanine chloride and the synthesis of boron subnaphthalocyanine chloride were the direct aim of this research. Axial ferrocenyl substitution is a desired modification to the subphthalocyanine core because ferrocenyl groups are excellent electron donors. The reaction scheme for the synthesis of axially substituted subphthalocyanine is described in scheme 1.



Scheme 1: Synthesis of axially substituted subphthalocyanine

Subnaphthalocyanines are similar to subphthalocyanines. The only difference is the extra aromatic ring of the dinitrile used for synthesis. They share many of the electronic properties of subphthalocyanines. The reaction scheme for the synthesis of boron subnaphthalocyanine chloride is described in scheme 2.



Scheme 2: Synthesis of boron subnaphthalocyanine chloride

UV- Vis Spectra:

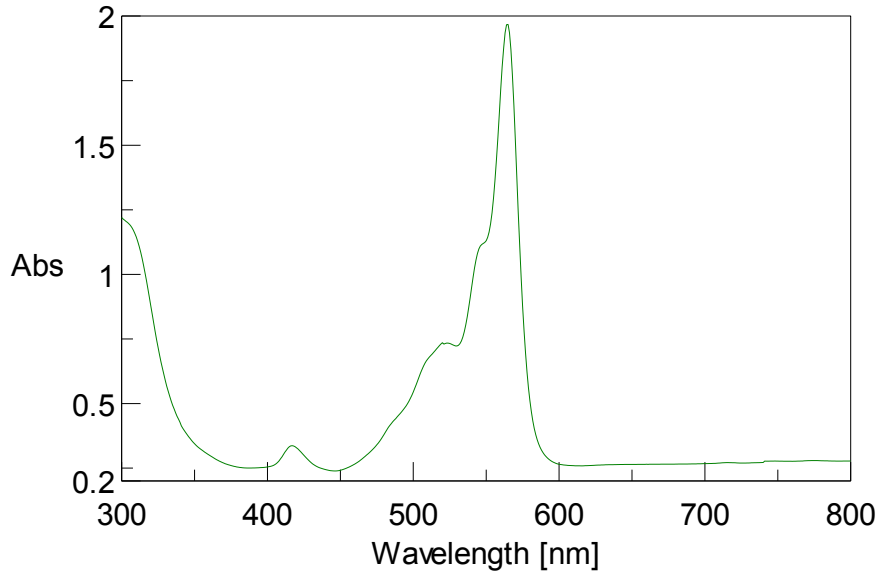


Figure 2: UV-Vis spectra axially-substituted subphthalocyanine

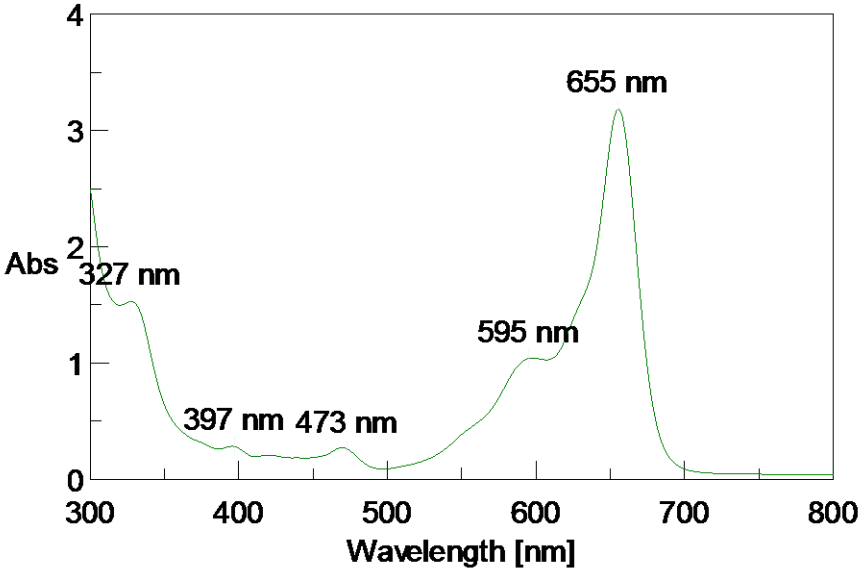


Figure 3: UV-Vis spectra subnaphthalocyanine

The UV-Vis spectra shows that the correct product was likely obtained in each reaction, indicated by the characteristic subphthalocyanine peak and associated shoulder in the 500-700 nm region. The UV-Vis spectrum of axially substituted subphthalocyanine is essentially identical to the UV-Vis spectrum of subphthalocyanine itself. Subnaphthalocyanine has a similar UV-Vis spectrum to subphthalocyanine, but is red-shifted by approximately 90 nm. This is due to the increased π-system due to the extra aromatic rings on each of the three sub-units of the molecule. This is also why subphthalocyanine appears blue and subnaphthalocyanine is pink in color.

Conclusion:

Based on UV-Vis spectra, the correct products were likely obtained in reaction schemes 1 and 2, giving percent yields of 17% and 53%, respectively. These products can be used for further applications in studying their electronic properties in donor-acceptor systems in an effort to find efficient systems for mimicking natural photosynthesis.

References:

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